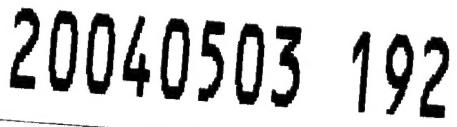


# REPORT DOCUMENTATION PAGE

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# Polynitrogen Chemistry: Recent Development in Pentazole and Polyazide Chemistry



Ashwani Vij

Space and Missile Propulsion Division  
Air Force Research Laboratory/PRSP  
Edwards AFB, CA 93524  
ashwani.vij@edwards.af.mil  
(661) 275-6278

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## Why Polynitrogen Compounds ?



- Polynitrogen compounds contain only nitrogen atoms and are expected to have unusual properties. Most important among these are:
  - *High endothermicity*
  - *"Green" propellant*  
*"combustion" product is only gaseous N<sub>2</sub>*
  - *High density*
  - *High I<sub>sp</sub> values when compared to other monopropellants or bipropellants*

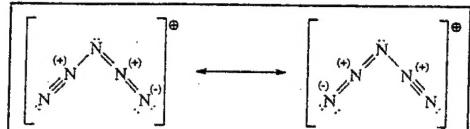
 *High detonation velocity*

## Geometry of the $N_5^+$ cation

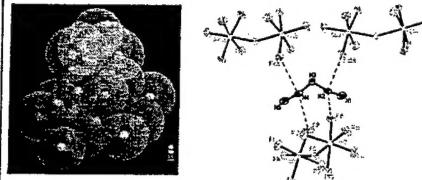
**V-Shaped Geometry**

**Calculated Structure**

**Experimental Structure**



**Resonance Structure**



N2 makes contacts at 2.723 and 2.768 Å  
N4 contacts are at 2.887 and 2.814 Å

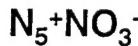
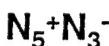
C&E News, 2000, 78, 41

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## (In)Compatibility of $N_5^+$

Attempts to couple  $N_5^+$  with energetic anions can result in explosive reactions !!!



Our goal is the synthesis of an "aromatic" polynitrogen anion with

- A high first ionization potential
- A high activation energy barrier towards decomposition

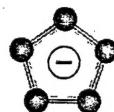
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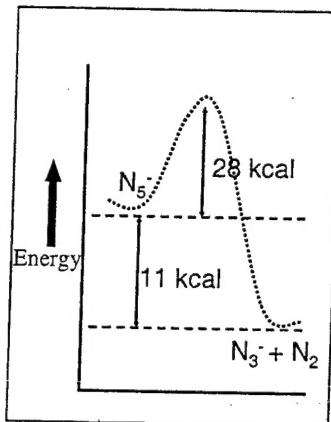


## New Polynitrogen Anions as Counterparts for $N_5^+$



Pentazole anion ( $N_5^-$ )

- Theoretical calculations show that this anion has a 28 kcal/mole activation energy barrier for decomposition and its decomposition to  $N_3^-$  and  $N_2$  is only 11 kcal/mol exothermic
- Free pentazole has not been isolated to date. Only aryl substituted pentazoles can be isolated and stabilized at low temperatures. These compounds rapidly decompose above 273K to form aryl azides and  $N_2$  gas



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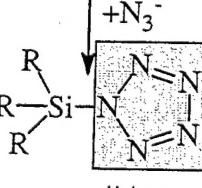
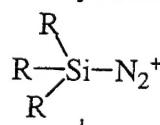
## Synthetic Challenge – How do we make These New Anions??



### Synthesis of Substituted Pentazoles

#### Sources for the Pentazole Anion ( $N_5^-$ )

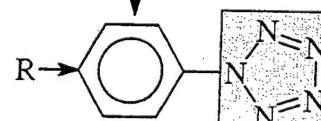
Silyl Diazonium Salts



Aryl Diazonium Salts



R = electron releasing group



I. Ugi, Angew. Chem., 1961, 73, 172

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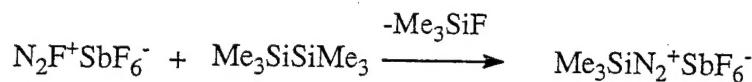
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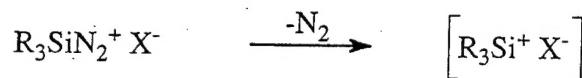
## Formation and Stability of Silyl Diazonium Salts



- Failed attempts to synthesize silyl diazonium salts



- $\text{R}_3\text{SiN}_2^+$  salts are unstable and spontaneously lose  $\text{N}_2$



*Theoretical calculations support this experimental observation.*

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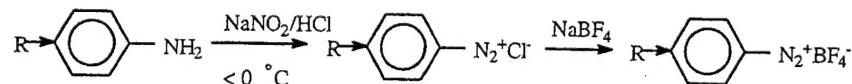
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## Synthesis of Aryldiazonium Salts

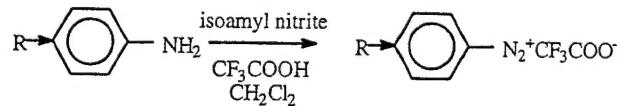


### Aqueous Media



$\text{R} = \text{H}, \text{OH}, \text{OCH}_3, \text{OC}_6\text{H}_5, \text{OC}_6\text{H}_4\text{N}_2^+, \text{N}(\text{CH}_3)_2$

### Non-aqueous Media



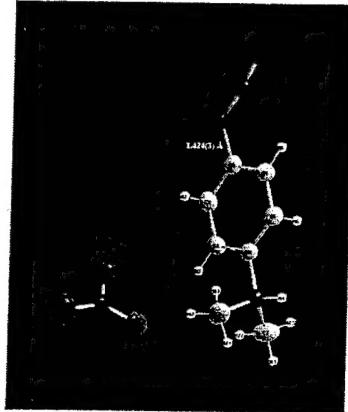
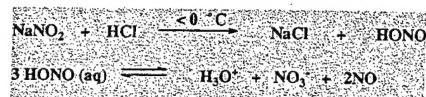
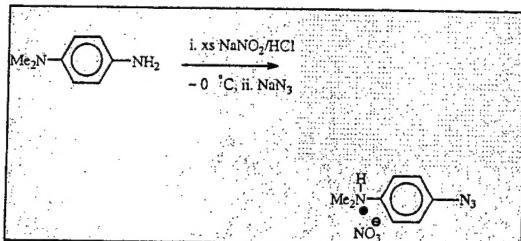
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## Pentazole Formation... Not a Trivial Chore !!!



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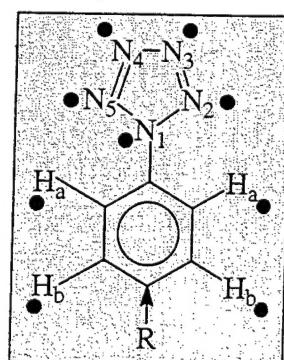


## Identification of Arylpentazoles



Pentazoles can be characterized by low temperature NMR spectral studies using  $^{15}\text{N}$  labeled samples.

- $^1\text{H}$  NMR: AB-type spectrum with  $\text{H}_a$  and  $\text{H}_b$  at 8.0 and 7.0 ppm
- $^{14}\text{N}$  NMR:  $\text{N}_1$  at  $\sim -80$  ppm
- $^{15}\text{N}$  NMR:  $\text{N}_2/\text{N}_5$  at  $\sim -27$  ppm and  $\text{N}_3/\text{N}_4$  at  $\sim -4$  ppm



Note: Qualitative evidence for the presence of a pentazole ring:  $\text{N}_2$  gas evolution in solution

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## **Cleavage of the Aryl-Pentazole Bond with Retention of the Pentazole Ring**



- Chemical Methods

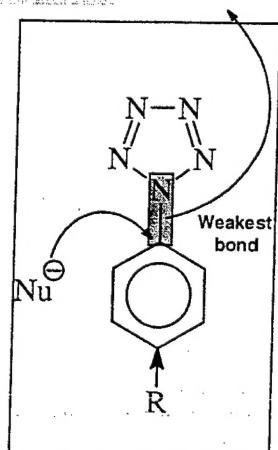
➤ Ozonolysis does not work! (Ugi, Radziszewski)

V. Benin, P. Kszysinski and G. J. Badziszewski / Org. Chem. 2002, 67, 1251

- Nucleophilic substitution using strong nucleophiles such as the  $\text{OH}^-$ ,  $\text{OR}^-$ ,  $\text{F}^-$  etc.

- Collisional Fragmentation (ElectroSpray Ion Mass Spectroscopy – ESIMS)

- Electrospray is very gentle and produces high concentration of the parent anion which can be mass selected
- Negative ion detection eliminates interference from neutral or positively charged species.

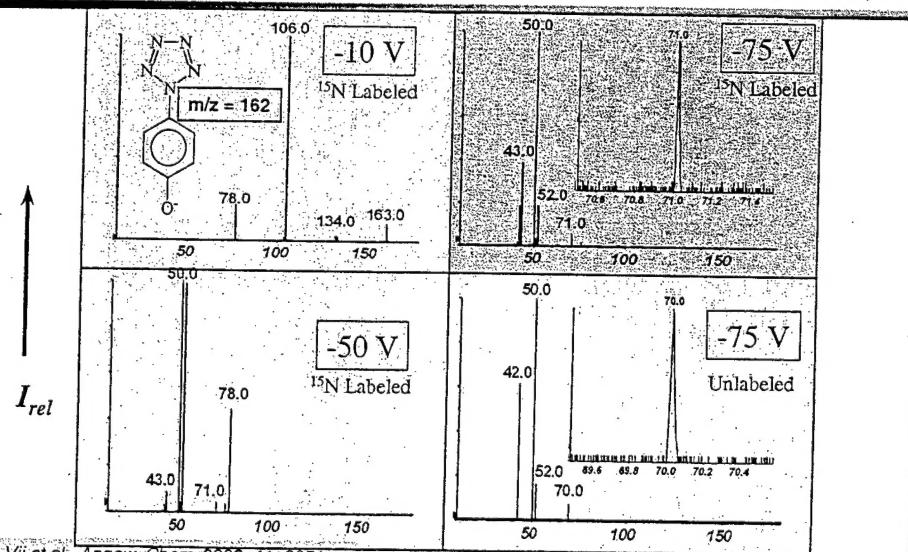


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## MSMS of the Parent Ion Peak



Vij et al., Angew. Chem. 2002, 41, 3051

*m/z*

C&E News, 2002, 80, 8

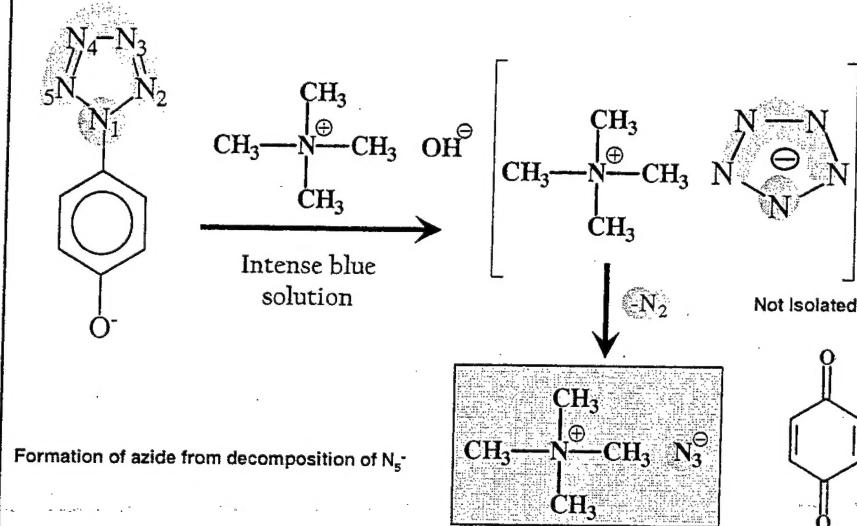
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## Chemical Cleavage of the C-N Bond

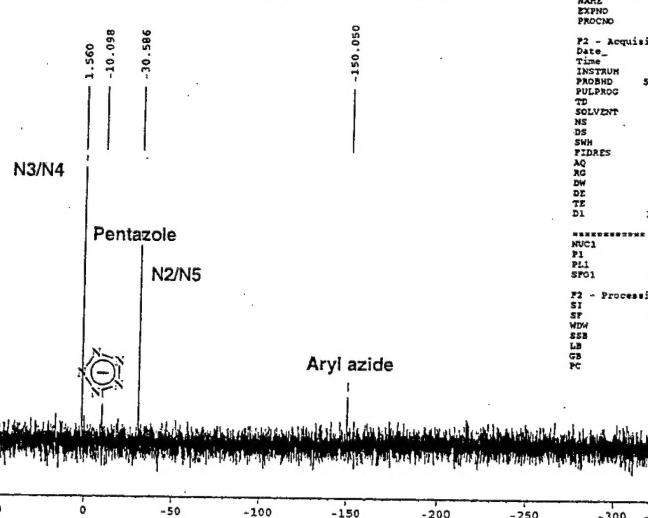


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## Aryl-pentazole bond cleavage: $N_5^-$ anion in Solution



1BN Labeled HCC64NB in AN/CDC/C12 + TBACH  
15N NMR at -30 C, SR = 15576.07

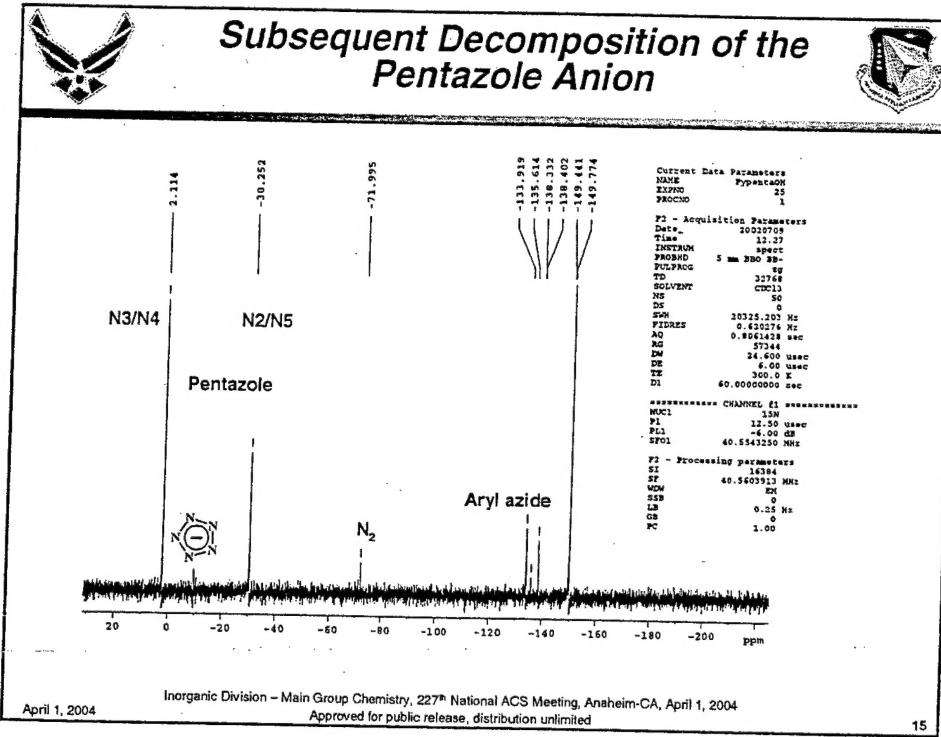
Current Data Parameters	
NAME	Pyrazole
EXPN0	0
PROCNO	1
P2 - Acquisition Parameters	
DATE	20020708
TIME	15:02
TECO	1.00 sec
PROBHD	5 mm BBG BB
PULPROG	90
TD	32768
SOLVENT	CDCl3
NS	31
DS	0
SWH	20395.203 Hz
ETRATES	0.52000 Hz
AQ	0.0041428 sec
RG	4
DW	24.00 usec
DE	6.00 usec
TE	300.0 X
DI	10.0000000 sec
***** CHANNEL 1 *****	
NUC1	15N
FI	12.50 usec
PL1	-1.00 dB
SP1	40.5542317 MHz
P2 - Processing parameters	
SI	16384
SF	40.5604931 MHz
WDW	ZH
SSB	0
LB	0.25 Hz
GS	0
PC	1.00

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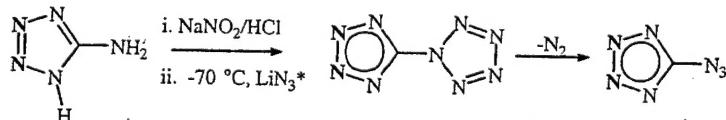
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## *Subsequent Decomposition of the Pentazole Anion*



## *Pentazoles with Heterocyclic Substituents*

- Tetrazolyl system is unstable above -70 °C and the pentazole ring rapidly decomposes to liberate N<sub>2</sub> gas.

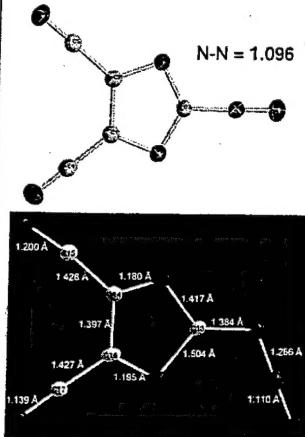
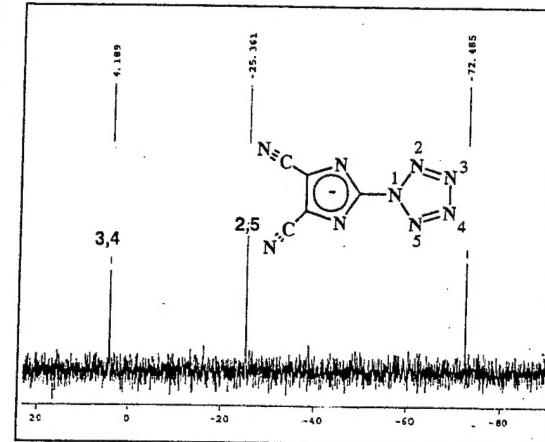


A. Hammerl and T. M. Kläpoetke, *Inorg. Chem.* 2002, 41, 906-912

- In comparison, the pentazole ring derived from 2-amino-4,5-dicyanoimidazole shows higher thermal stability (-30 °C)



## $^{15}\text{N}$ NMR of 2-pentazolyl-4,5-dicyano-imidazole



$^{15}\text{N}$  NMR recorded in a mixture of methanol and acetonitrile at  $-30^\circ\text{C}$ , nitromethane used as an external reference (0 ppm)

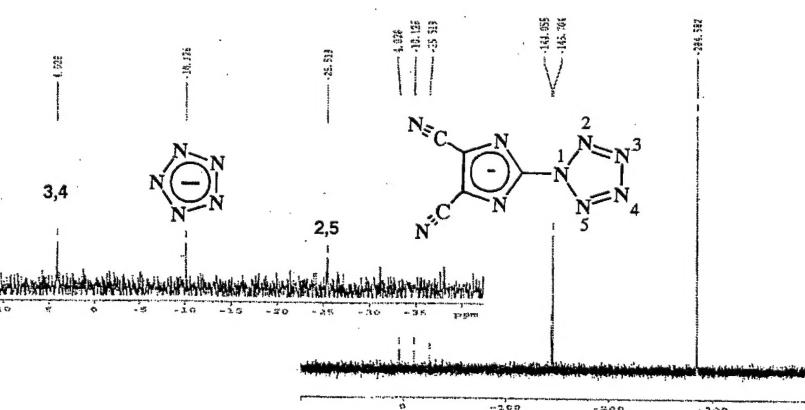
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## Pentazolate Anion in Solution ?



➤  $^{15}\text{N}$  NMR shows a peak at  $\sim -10$  ppm ( $-30^\circ\text{C}$ ) upon addition of base, which slowly decomposes to form  $\text{N}_2$  and azide ion.

➤ This peak is also observed upon adding a base to the solution of arylpentazoles at  $-30^\circ\text{C}$ .

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## Chronology of the Pentazolate Anion



➤ ESIMS of *para*-hydroxyphenylpentazole

Vij, Pavlovich, Wilson, Vij, Christe, Angew. Chem. Int'l. Ed. Engl 2002, 41, 3051  
Submitted: April 30, 2002; accepted July 3, 2002

➤  $^{15}\text{N}$  NMR studies showing a peak at -10.2 ppm (-40 °C) due to the Pentazole anion resulting from cleavage of *para*-methoxyphenylpentazole which slowly decomposes to form N<sub>2</sub> and azide ion. Upon standing for several days, all peaks disappear!

Butler, Stephens & Burke, Chem. Commun. 2003, 1016  
Submitted: February 6, 2003; accepted February 27, 2003

➤ Laser Desorption Ionization (LDI) time-of-flight (TOF) mass spectrometry of solid *para*-*N,N*-dimethylaminophenylpentazole shows peaks at m/z: 70 ( $\text{N}_5^-$ ) and -42 ( $\text{N}_3^-$ ). Peak at 70 confirmed by  $^{15}\text{N}$  labeling experiment.

Ostmark, Wallin, Brinck, Carlqvist, Claridge, Hedlund & Yudina, Chem. Phys Lett., 2003, 379, 539  
Submitted: Jun. 27, 2003; accepted August 27, 2003

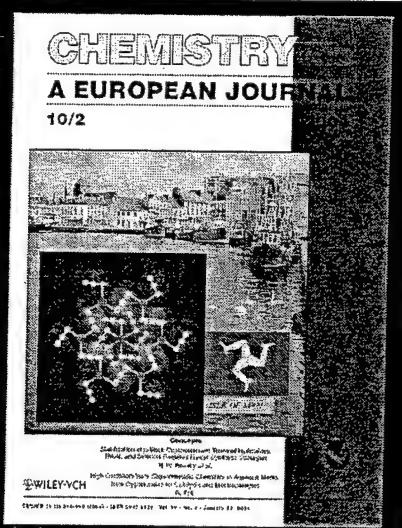
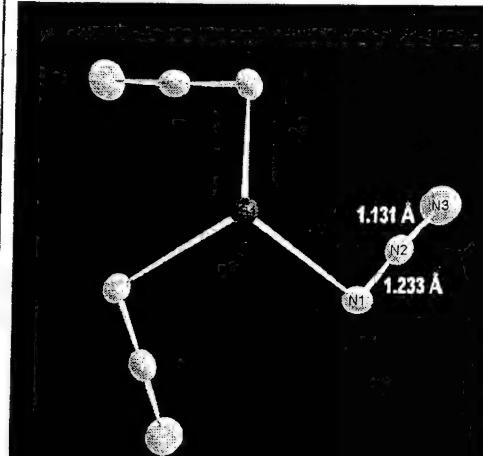
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## What are “normal” N-N distances in azides?



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## *Abnormalities in azide distances: Artifacts or Structural Contaminants?*



- ✓ A large number of crystal structures reported in Cambridge/Inorganic CSD report unusually short  $N_{\alpha}\text{-}N_{\beta}$  (0.8- 1.0 Å) and long  $N_{\beta}\text{-}N_{\gamma}$  (1.2-1.4) distances.

According to VB theory, in covalently bonded azides,  
 $N_{\alpha}\text{-}N_{\beta} > N_{\beta}\text{-}N_{\gamma}$

Wolfgang, F. and Klapoetke, T. In *Inorganic Chemistry Highlights*; Meyer, G., Naumann, D. and Wesemann, L. Eds.; Wiley-VCH: Weinheim, 2002, Chapter 16 and references therein

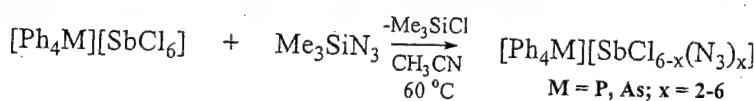
- ✓ In most cases, these derivatives were prepared from metal chloride salts and/or recrystallized from chlorinated solvents

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## *Reactivity of hexachloroantimonate (VI) with Trimethylsilylazide*



- ✓ The substitution of all the six chlorine atoms in  $\text{SbCl}_6^-$  by the azide groups could not be accomplished in a single step, as reported in literature. The stepwise substitution gives a good insight into the substitution mechanism.

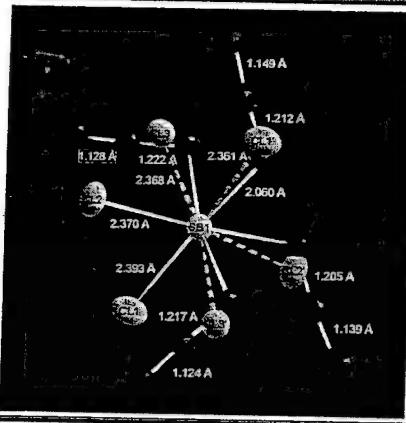
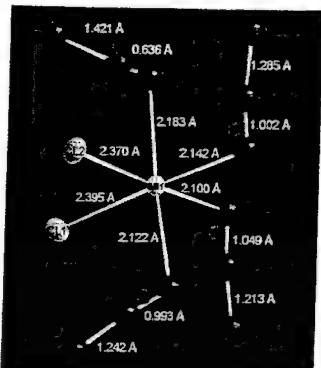
- ✓ Total substitution was achieved after four “refreshment” cycles of the reagents. During the intermediate cycles, the azide content gradually increased from two to five.

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## The tetraphenylarsonium antimonychloride azide case



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## Summary



- Synthesized aryl pentazoles: hydroxy group at the *para*-position on the aryl ring gives the best results as observed during this study.
- Demonstrated selective cleavage of C-N bond by ESIMS with retention of pentazole ring. Results confirmed studying  $^{15}\text{N}$  labeled pentazoles.
- Experimental detection of pentazolate anion in solution using different substrates.
- Offers potential pathway for bulk synthesis of  $\text{N}_5^-$  salts
- Chloride ion cause abnormalities in N-N bonds in azides

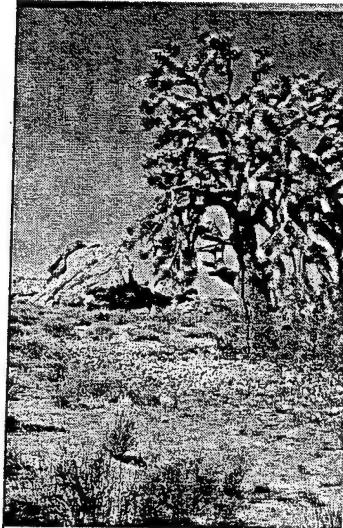
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## Acknowledgments



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Dr. James Pavlovich (UCSB)



Dr. Robert Corley, Dr. Ronald Channell, Mr. Michael Huggins (AFRL)

\$\$\$

Dr. Don Woodbury, Dr. Arthur Morrish (DARPA)

Dr. Michael Berman (AFOSR)

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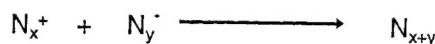
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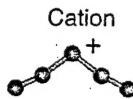
## Recipe for Synthesizing Neutral Polynitrogen Compounds



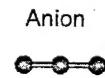
- Combine a polynitrogen cation with a polynitrogen anion to form a neutral polynitrogen compound.



ONLY TWO STABLE POLYNITROGEN IONS KNOWN TO EXIST IN BULK



$N_5^+$  cation  
(discovered in 1999, AFRL, Christe)



$N_3^-$  anion  
(discovered in 1890, Curtius)

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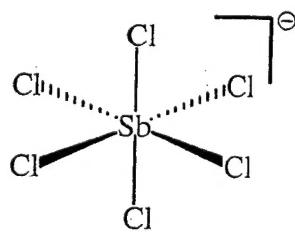
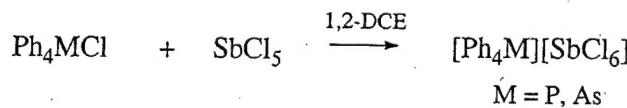
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## Episode I...Generation of the starting material



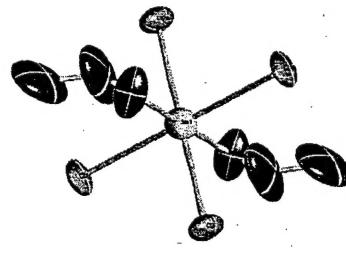
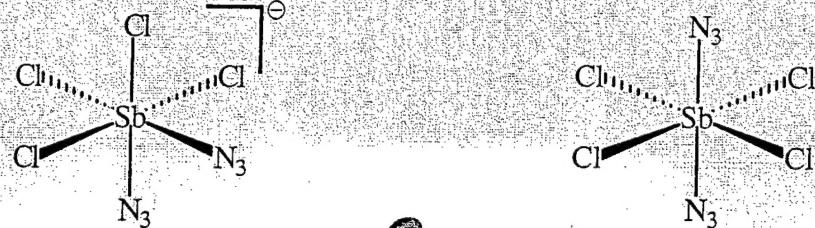
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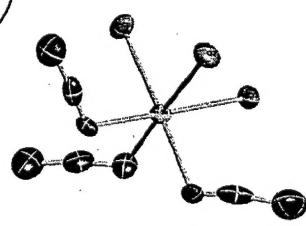
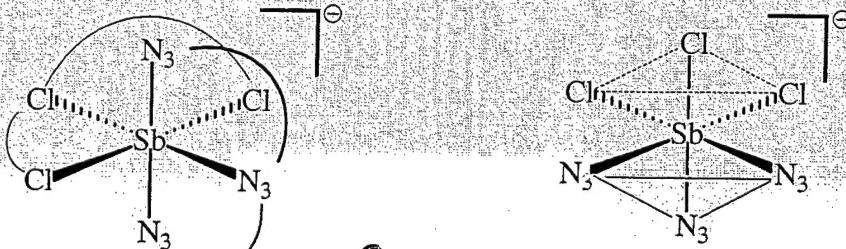
**Episode II....cis- or trans- disubstitution  
with azide groups?**



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**Episode III...Substitution of 3<sup>rd</sup> chlorine...  
fac- or mer- isomer ???**



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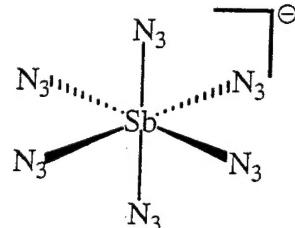
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## Episode VI...Complete substitution of chlorine atoms



No crystal structure obtained yet. However, IR and Raman spectroscopy shows that Sb-Cl bonds are absent i.e., complete substitution by the azide groups.



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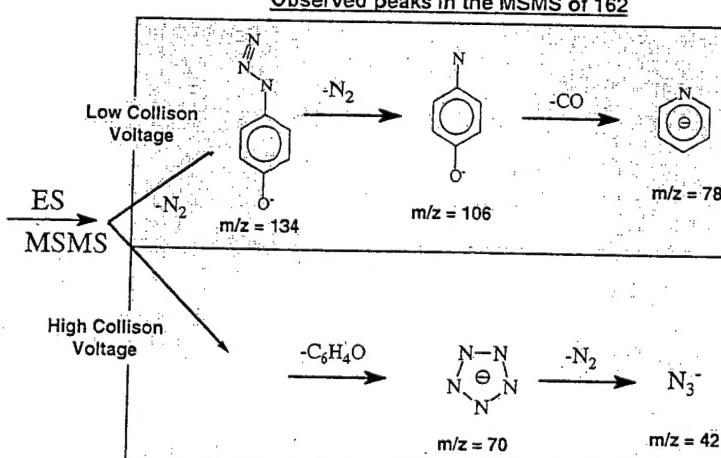
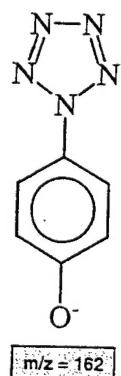
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## ESIMS of para-Phenoxypentazole



### Observed peaks in the MSMS of 162

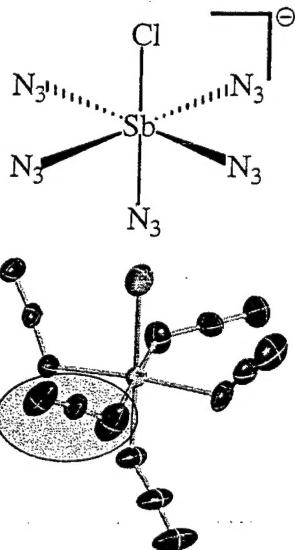


Vij, Pavlovich, Wilson, Vij & Christe, *Angew. Chem. Int. Ed.* 2002, 41, 3051-3054  
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**Episode V: Synthesis of  
Chloropentaazidoantimonate(VI) Anion**



**The Structure of  $\text{Ph}_4\text{PSbCl}(\text{N}_3)_5$**

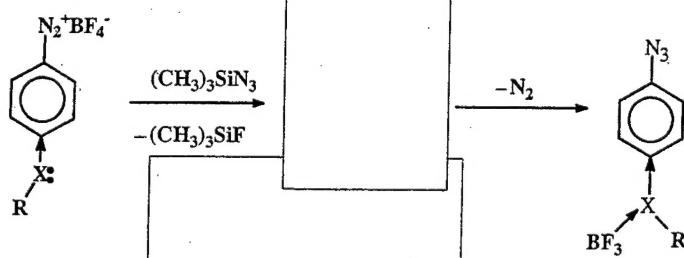
- ✓ The crystals grown from  $\text{CH}_3\text{CN}$
- ✓ Triclinic space group  $P-1$
- ✓ Cell constants:  $a = 11.134(3)\text{ \AA}$ ,  $b = 11.663(3)\text{ \AA}$ ,  $c = 13.754(4)\text{ \AA}$ ;  $\alpha = 104.314(5)^\circ$ ;  $\beta = 97.914(5)^\circ$ ;  $\gamma = 115.807(4)^\circ$
- ✓  $Z = 2$
- ✓  $R = 0.0762$
- ✓ All azide distances "normal" except  $\text{N}10-\text{N}11-\text{N}12$

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**Reaction with Trimethylsilyl Azide**



X= N, O

**No pentazoles were isolated !!!**

Reactions carried out in acetonitrile at -30 °C

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